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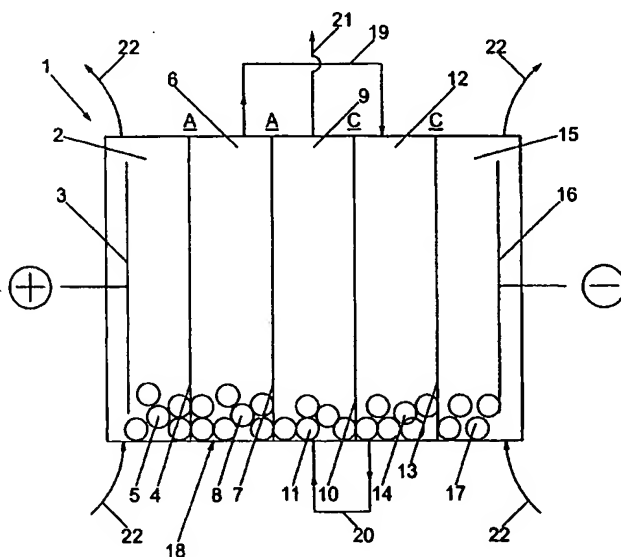
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(54) Title: ELECTRODEIONISATION APPARATUS



(57) Abstract: An electrodeionisation apparatus comprising, successively: means defining an anode chamber, means defining one or more anion exchange chambers, means defining one or more mixed exchange chambers, means defining one or more cation exchange chambers, and means defining a cathode chamber, the anion, mixed and cation exchange chambers providing a flow path for water to be purified, is described. The present invention incorporates advantages of both separate resin bed and mixed resin bed technology.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

1 Electrodeionisation Apparatus

2

3 The present invention relates to an
4 electrodeionisation apparatus for purifying water
5 and method therefor.

6

7 Apparatus and methods for electrodeionisation to
8 provide purified water are well known, see for
9 example our GB-A-2311999 and US 4687561. Generally,
10 water to be purified is passed along a deionising
11 path set between an anode and a cathode. The
12 application of a potential difference between the
13 anode and cathode causes anions and cations in the
14 impure water to migrate towards their respective
15 attracting electrodes through perm-selective
16 membranes.

17

18 In general, such apparatus has the chambers for
19 exchanging anions and cations juxtapositioned so
20 that the anions and cations removed from the water
21 being purified both travel towards one or more
22 'concentrating' chambers, through which a desalting

1 stream flows to remove the unwanted anions and
2 cations.

3

4 It is an object of the present invention to provide
5 a simplified electrodeionisation apparatus and
6 method.

7

8 According to one aspect of the present invention,
9 there is provided an electrodeionisation apparatus
10 comprising, successively:

11

12 means defining an anode chamber,
13 means defining one or more anion exchange chambers,
14 means defining one or more mixed exchange chambers,
15 means defining one or more cation exchange chambers,
16 and
17 means defining a cathode chamber,

18

19 the anion, mixed and cation exchange chambers
20 providing a flow path for water to be purified.

21

22 By locating the or each anion exchange chamber next
23 to the anode chamber, and locating the or each
24 cation exchange chamber next to the cathode chamber,
25 the apparatus of the present invention provides an
26 opposite or reverse flow-path for exchanged anions
27 and cations than prior apparatus. The exchanged
28 anions and cations in the water being purified are
29 directly attracted to neighbouring electrodes,
30 rather than being attracted to distal electrodes
31 located across opposing exchange chambers of prior
32 electrodeionisation apparatus.

1 In one embodiment of the present invention, the
2 apparatus involves one anion exchange chamber and
3 one cation exchange chamber.

4
5 Located between the chambers are perm-selective
6 membranes as are known in the art. Those membranes
7 located between the or each central mixed exchange
8 chamber and the cathode chamber should be cation
9 membranes, and those membranes located between the
10 or each mixed exchange chamber and the anode chamber
11 should be anion membranes.

12
13 Preferably, the or each anion exchange chamber
14 partly, substantially or wholly contains anion
15 exchange material, and the or each cation exchange
16 chamber partly, substantially or wholly contains
17 cation exchange material.

18
19 Preferably, the anode chamber partly, substantially
20 or wholly contains ion exchange material, preferably
21 cation exchange material. Preferably, the cathode
22 chamber, partly, substantially or wholly contains
23 ion exchange material, more preferably cation
24 exchange material. Also preferably, the or each
25 mixed exchange chamber partly, substantially or
26 wholly contains mixed ion exchange material. Ion
27 exchange materials are known in the art, one example
28 being resin beads.

29
30 The anode and cathode chambers are preferably
31 flushed with a desalting stream such as water to
32 elute ions from the system as concentrate.

1 In another embodiment of the present invention,
2 water to be purified is firstly passed through an
3 anion exchange chamber of the apparatus, then
4 through a cation exchange chamber, and subsequently
5 through a mixed exchange chamber.

6
7 Alternatively, water to be purified is passed
8 through a cation exchange chamber, then through an
9 anion exchange chamber, and subsequently through a
10 mixed exchange chamber.

11
12 Where apparatus of the present invention involves
13 two or more anion exchange chambers and/or two or
14 more cation exchange chambers and/or two or more
15 mixed exchange chambers, then impure water flow path
16 could be directed through subsequent anion exchange
17 chambers and/or subsequent cation exchange chambers
18 and/or subsequent mixed exchange chambers in the
19 same or any suitable or relevant order.

20
21 In a third embodiment of the present invention,
22 water to be purified by the present apparatus is
23 combined with already purified water, so reducing,
24 by dilution, the load on the exchange materials.
25 The already purified water may be provided from a
26 separate source, or be provided by re-circulating
27 outflow from the present apparatus, which outflow
28 could be temporarily held in a reservoir such as a
29 holding tank.

30

31 According to a fourth embodiment of the present
32 invention, the anion, cation and mixed exchange

1 chambers are relatively thick compared with chambers
2 of prior art electrodeionisation apparatus. The
3 simplicity of the present invention allows thicker
4 chambers and beds of ion exchange materials to be
5 used, compared with the conventional view that
6 thinner beds are necessary to maintain electric
7 current flow thereacross.

8
9 The present invention also extends to a 'multiple'
10 unit still only involving one set of electrodes.
11 For example, the unit could be arranged: anode
12 (chamber), anion, mixed, cation, concentrate...,
13 anion, mixed, cation, concentrate..., anion, mixed,
14 cation, cathode.

15
16 According to a second aspect of the present
17 invention, there is provided a method of
18 electrodeionisation comprising causing or allowing
19 water to be purified to flow through an anion
20 exchange chamber neighbouring an anode chamber,
21 followed by flow through a cation exchange chamber
22 neighbouring a cathode chamber, or vice versa,
23 followed by flow through a mixed exchange chamber
24 located between the anion exchange chamber and the
25 cation exchange chamber.

26
27 The method of the present invention could use
28 electrodeionisation apparatus as described above.
29 In the method of the present invention, the water to
30 be purified could be pre-mixed with a proportion of
31 already purified water.

32

1 In general, water may be passed through each chamber
2 independently, allowing different flow rates,
3 including no flow, at different times.

4

5 An embodiment of the present invention will now be
6 described by way of example only, and with reference
7 to the accompanying drawing, Figure 1, which is a
8 schematic cross-sectional side view of apparatus
9 according to the present invention.

10

11 Referring to the drawing, Figure 1 shows an
12 electrodeionisation apparatus in the form of a stack
13 (1). The stack (1) has five chambers. The first
14 chamber (2) is an anode chamber bounded on one side
15 by an anode (3) and on the other by an anion
16 membrane (4). The anode chamber (2) contains cation
17 exchange resin beads (5). Juxtaposed the anode
18 chamber (2) is an anion exchange chamber (6) bounded
19 on one side by the anion membrane (4), and on the
20 other side by a second anion membrane (7). The
21 anion exchange chamber (6) contains anion exchange
22 resin beads (8). Next to the anion exchange chamber
23 (6) is a mixed exchange chamber (9), bounded by the
24 second anion membrane (7) and a cation membrane
25 (10). This chamber (9) contains mixed ion exchange
26 resin beads (11).

27

28 Juxtaposed the mixed exchange chamber (9), there is
29 a cation exchange chamber (12) bounded by the cation
30 membrane (10), and a second cation membrane (13).
31 The cation exchange chamber (12) contains cation
32 exchange resin beads (14).

1 Juxtaposed the cation exchange chamber (12) lies a
2 cathode chamber (15) bounded by the second cation
3 exchange membrane (13) and a cathode (16). The
4 cathode chamber (15) contains cation exchange resin
5 (17).

6
7 The nature and form of the electrodes, membranes and
8 ion exchange materials are all known in the art.

9
10 In use, impure feed water (18) enters the stack (1),
11 and firstly enters the anion exchange chamber (6).
12 The anion exchange resin beads (8) in this chamber
13 (6) replace the anions in the feed water with
14 hydroxide ions from the resin beads (8). The anions
15 then move towards and through the anion exchange
16 membrane (4) to the anode chamber (2). The driving
17 force for this movement is an electrical potential
18 placed between the anode (3) and cathode (16). The
19 feed water (19) exiting this chamber (6) is then
20 passed into the cation exchange chamber (12), where
21 the cation exchange resin beads (14) exchange
22 cations in the feed water for hydrogen ion. The
23 cations then move towards and through the cation
24 exchange membrane (13) to the cathode chamber (15).

25
26 The water (20) exiting this chamber (12) is then
27 passed into the mixed resin chamber (9). The mixed
28 resin beads remove both anionic and cationic ions
29 that have passed through the first two chambers (6,
30 12). Ions removed in the mixed exchange chamber (9)
31 pass through the relevant ion exchange membranes (7,
32 10) to the single exchange chambers, where they, as

1 well as ions exchanged therein, pass through the
2 relevant ion exchange membranes into the electrode
3 compartments.
4

5 From the mixed chamber (9) final product water (21)
6 is obtained for use.
7

8 The electrode compartments (2, 15) are flushed with
9 water to elute the ions from the system as
10 concentrate (22). This flow may be in series or in
11 parallel.
12

13 In an alternative arrangement, feed water could
14 firstly be passed into the cation exchange chamber
15 (12), followed by the anion exchange chamber (6),
16 before being passed into the mixed exchange chamber
17 (9). This alternative flow-path arrangement also
18 allows the removal of precipitative cations such as
19 calcium before they reach the anion exchange
20 material (8) and anion membranes (4, 7) on which
21 they are likely to precipitate. As these ions pass
22 into the cathode exchange chamber (12), it is
23 preferable to maintain a low pH in the cathode
24 exchange chamber (12) and to feed the cathode
25 chamber (15) with water, or acid, devoid of
26 precipitative ions.
27

28 The product water (21) exiting the mixed exchange
29 chamber (9) of the present invention has been found
30 to be of low ionic content. Indeed, the flow rate
31 and purification achieved by the present invention
32 is comparable with prior art EDI apparatus, which

1 generally involves a significantly more complex
2 arrangement of chambers.

3

4 In another arrangement of the present invention, the
5 feed water (18) is pre-mixed with a proportion of
6 already purified water (21). By diluting the load
7 (i.e. concentration of impure ions to be removed
8 from the water), a higher flow rate through the
9 apparatus can be achieved.

10

11 Indeed, a ratio of 10:1 of already purified
12 water:impure water allows a flow rate of at least
13 2/3 litres per minute through the apparatus shown in
14 Figure 1. The already purified water could be
15 supplied from a separate source, or be re-circulated
16 product water (21) from the present apparatus.

17

18 The following test data using a design of stack as
19 shown in Figure 1 confirms the benefit of the
20 present invention:

21

22 Example 1

23

24 A stack with internal plate dimensions 150 mm x 66
25 mm x 15 mm was operated on a blend of reverse
26 osmosis permeate and deionised water. With a feed
27 of conductivity 18.2 $\mu\text{S}/\text{cm}$ (adjusted to 25°C) the
28 stack purified 0.55 litres per minute to a
29 conductivity of 0.073 $\mu\text{S}/\text{cm}$ when a current of 1.3
30 amps was applied between the electrodes. With a
31 feed of 7.2 $\mu\text{S}/\text{cm}$, 1.37 litres per minute were
32 purified to 0.092 $\mu\text{S}/\text{cm}$ at 1.3 amps.

1 Example 2

2

3 A stack with dimensions 135 mm x 68 mm x 10 mm was
4 operated recirculating from a tank. Water was
5 intermittently taken off after the stack and extra
6 make up was fed to the stack from a reverse osmosis
7 membrane. The applied current was 3.16 amps. When
8 the reverse osmosis unit was operating the feed to
9 the stack was 12.5 $\mu\text{S}/\text{cm}$ and this was purified at a
10 rate of 1.95 litres per minute to 0.062 $\mu\text{S}/\text{cm}$. When
11 recirculating from the tank the feedwater reduced in
12 conductivity to 0.32 $\mu\text{S}/\text{cm}$ at which time the product
13 water was 0.057 $\mu\text{S}/\text{cm}$.

14

15 The present invention incorporates advantages of
16 both separate resin bed and mixed resin bed
17 technology. Separate resin beds are beneficial for
18 removing known amounts of defined ionic impurity
19 types, both anion and cation, and the current
20 passing through that resin bed can be utilised in
21 removing solely that type of ion.

22

23 If the feed water is first passed through a cation
24 exchange resin bed, cations can be removed from the
25 solution causing a reduction in the solution pH.
26 Similarly, an anion resin bed will increase the pH.
27 Changes in pH help to prevent bacterial growth, and
28 may also be used to prevent precipitation, or
29 increase the ionic nature of weakly charged species.

30

1 Meanwhile, mixed resin beds have been noted to
2 handle high flow rates of water whilst still
3 achieving high levels of purification.

4

5 The present invention has several further
6 advantages. It provides a compact purification unit
7 using a single set of electrodes. It is of simple
8 form, allowing simplified manufacturing thereof,
9 with less complication and therefore with reduced
10 risk of potential breakdown.

11

12 As mentioned before, water may be passed through
13 each chamber independently, allowing different flow
14 rates, including no flow, at different times.

15

16 Also, the number of chambers of the present
17 invention, possibly being only five, are less than
18 many prior art apparatus, thus reducing the problems
19 of back pressure on the feed water, and allowing a
20 faster flow rate therethrough. The use of
21 relatively thick chambers in the present invention
22 also reduces the feed water back pressure.

23

24 Furthermore, feed water through the present
25 invention does not pass through the anode or cathode
26 chambers as occurs in some prior art apparatus,
27 thereby avoiding the problem of gas in the product
28 water.

29

30 Also, the present invention aids removal of weakly
31 ionised species, and can be used in a manner to
32 inhibit precipitative fouling.

1 Claims

2

3 1. An electrodeionisation apparatus comprising,
4 successively:

5

6 means defining an anode chamber,

7 means defining one or more anion exchange

8 chambers,

9 means defining one or more mixed exchange

10 chambers,

11 means defining one or more cation exchange

12 chambers, and

13 means defining a cathode chamber,

14

15 the anion, mixed and cation exchange chambers

16 providing a flow path for water to be purified.

17

18 2. Apparatus as claimed in Claim 1 involving one
19 anion exchange chamber and one cation exchange
20 chamber.

21

22 3. Apparatus as claimed in Claim 1 or Claim 2
23 wherein two or more of the chambers are divided
24 by perm-selective membranes.

25

26 4. Apparatus as claimed in Claim 3 wherein any
27 membrane located between the or each central
28 mixed exchange chamber and the cathode chamber
29 is a cation membrane.

30

31 5. Apparatus as claimed in Claim 3 or Claim 4
32 wherein any membrane located between the or

- 1 each mixed exchange chamber and the anode
2 chamber is an anion membrane.
3
- 4 6. Apparatus as claimed in any one of the
5 preceding Claims wherein the or each anion
6 exchange chamber partly, substantially of
7 wholly contains anion exchange material.
8
- 9 7. Apparatus as claimed in any one of the
10 preceding Claims wherein the or each cation
11 exchange chamber partly, substantially or
12 wholly contains cation exchange material.
13
- 14 8. Apparatus as claimed in any one of the
15 preceding Claims wherein the anode chamber
16 partly, substantially or wholly contains ion
17 exchange material.
18
- 19 9. Apparatus as claimed in any one of the
20 preceding Claims wherein the cathode chamber,
21 partly, substantially or wholly contains ion
22 exchange material.
23
- 24 10. Apparatus as claimed in Claim 8 or Claim 9
25 wherein the ion exchange material is cation
26 exchange material.
27
- 28 11. Apparatus as claimed in any one of the
29 preceding Claims wherein the or each mixed
30 exchange chamber partly, substantially or
31 wholly contains mixed ion exchange material.
32

- 1 12. Apparatus as claimed in any one of Claims 6 to
2 11 wherein the ion exchange material is resin
3 beads.
4
- 5 13. Apparatus as claimed in any one of the
6 preceding Claims wherein the or each anion,
7 cation and/or mixed exchange chambers are
8 between 5-20mm wide.
9
- 10 14. A method of electrodeionisation comprising
11 causing or allowing water to be purified to
12 flow through an anion exchange chamber
13 neighbouring an anode chamber, followed by flow
14 through a cation exchange chamber neighbouring
15 a cathode chamber, followed by flow through a
16 mixed exchange chamber located between the
17 anion exchange chamber and the cation exchange
18 chamber.
19
- 20 15. A method of electrodeionisation comprising
21 causing or allowing water to be purified to
22 flow through a cation exchange chamber
23 neighbouring a cathode chamber, followed by
24 flow through an anion exchange chamber
25 neighbouring an anode chamber, followed by flow
26 through a mixed exchange chamber located
27 between the anion exchange chamber and the
28 cation exchange chamber.
29
- 30 16. A method as claimed in Claim 14 or claim 15
31 wherein the flow of water through each chamber
32 is independent of other flows.

- 1 17. A method as claimed in any one of Claims 14 to
2 Claim 16 wherein the anode and cathode chambers
3 are flushed with a desalting stream.
4
- 5 18. A method as claimed in any one of Claims 14 to
6 17 which involves two or more anion exchange
7 chambers and/or two or more cation exchange
8 chambers and/or two or more mixed exchange
9 chambers, wherein the water to be purified
10 flows through one or more subsequent anion
11 exchange chambers and/or one or more subsequent
12 cation exchange chambers and/or one or more
13 subsequent mixed exchange chambers in the same
14 or any suitable or relevant order.
15
- 16 19. A method as claimed in any one of Claims 14 to
17 18 wherein the water to be purified is combined
18 with purified water prior to
19 electrodeionisation.
20
- 21 20. A method as claimed in Claim 19 wherein the
22 water to be purified is combined with water
23 provided by outflow product of the method of
24 Claims 14 to 18.
25
- 26 21. A method as claimed in any one of Claims 14 to
27 20 wherein apparatus as claimed in any one of
28 Claims 1 to 13 is used.

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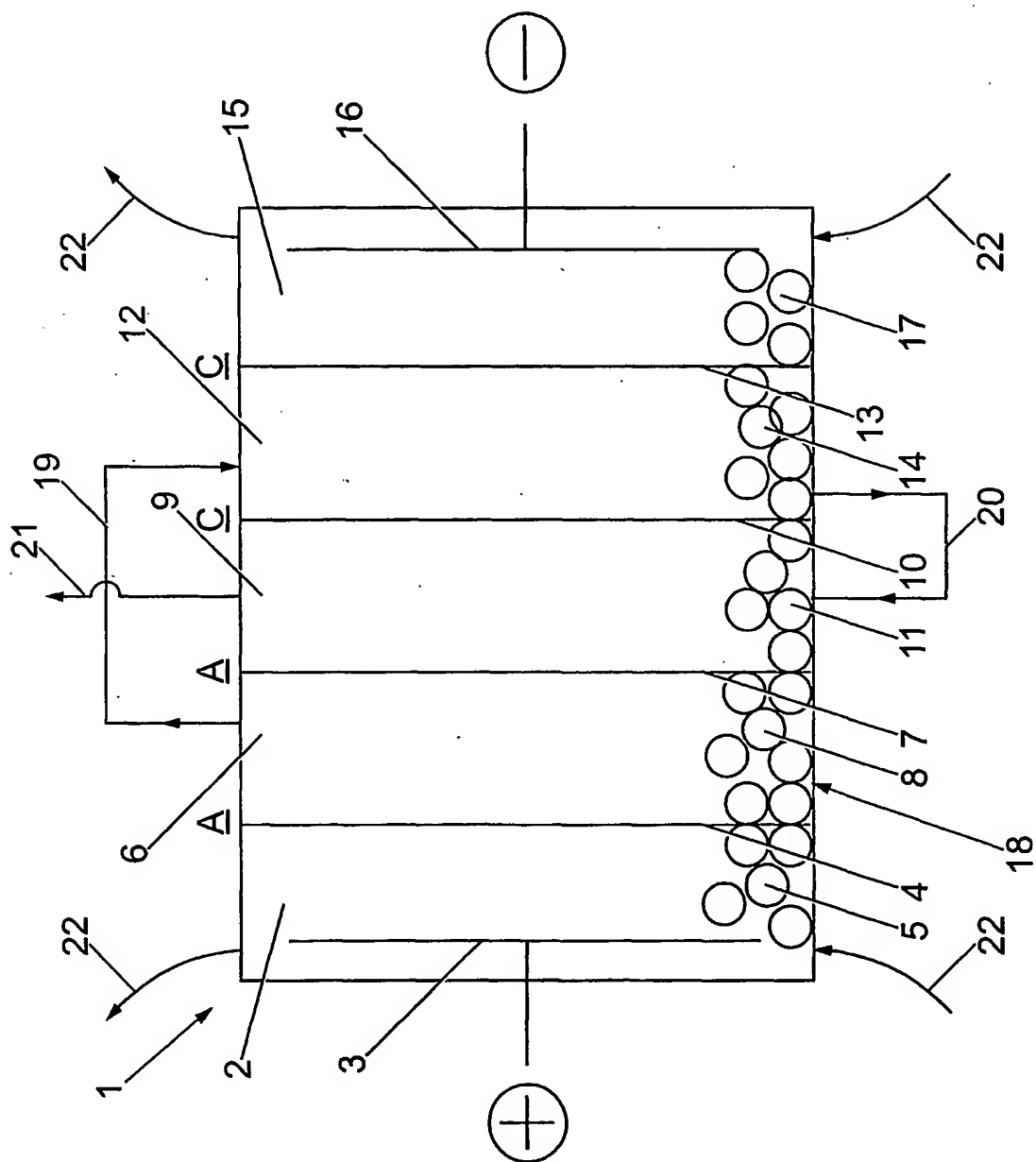


Fig. 1

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 32 38 280 A (LIEBER HANS WILHELM PROF DR IN) 19 April 1984 (1984-04-19) claims 1-3,5; figures 1,2,5	1-21
A	GB 2 311 999 A (ELGA GROUP SERVICES LTD) 15 October 1997 (1997-10-15) cited in the application claims 1,5; figure 1	1-21
A	US 4 687 561 A (KUNZ GERHARD) 18 August 1987 (1987-08-18) cited in the application claim 1.16; figure 1	1-21
A	US 3 869 376 A (TEJEDA ALVARO R) 4 March 1975 (1975-03-04) figure 5	1-21



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Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 3238280	A	19-04-1984	DE 3238280 A1	19-04-1984
GB 2311999	A	15-10-1997	DE 19713977 A1	30-10-1997
US 4687561	A	18-08-1987	DE 3217990 A1	17-11-1983
			DE 3241681 A1	17-05-1984
			DE 3241682 A1	17-05-1984
			AT 63479 T	15-06-1991
			AU 1557783 A	02-12-1983
			DE 3382286 D1	20-06-1991
			WO 8303984 A1	24-11-1983
			EP 0113387 A1	18-07-1984
			CA 1289103 A1	17-09-1991
US 3869376	A	04-03-1975	NONE	